

## SECTION 4.0

### EMISSIONS FROM BENZENE PRODUCTION

This section presents information on the four major benzene production source categories that may discharge benzene air emissions. The four major processes for producing benzene are:

- Catalytic reforming/separation;
- Toluene dealkylation and disproportionation;
- Ethylene production; and
- Coke oven light oil distillation.

For each of these production source categories, the following information is provided in the sections below: (1) a brief characterization of the national activity in the United States, (2) a process description, (3) benzene emissions characteristics, and (4) control technologies and techniques for reducing benzene emissions. In some cases, the current Federal regulations applicable to the source category are discussed. Table 4-1 lists U. S. producers of benzene and the type of production process used.<sup>11</sup>

Following the discussion of the major benzene production source categories, Section 4.5 contains a discussion of methods for estimating benzene emissions from process vents, equipment leaks, storage tanks, wastewater, and transfer operations. These emissions estimation methods are discussed in general terms and can be applied to the source categories in this section as well as the source categories in Section 5.0.

TABLE 4-1. BENZENE PRODUCTION FACILITIES

| Company Name   | Location                             | Annual Capacity<br>million gal<br>(million L) | Production Processes <sup>a</sup>  |
|--|--------------------------------------|---|--|
| Amerada Hess Corporation<br>Hess Oil Virgin Islands Corporation, subsidiary                | St. Croix, Virgin Islands            | 75 (284)                                      | Catalytic reformat; toluene; no captive use  |
| American Petrofina, Incorporated<br>Fina Oil and Chemical Company, subsidiary              | Port Arthur, Texas                   | 33 (125)<br>31 (117)                          | Catalytic reformat; partly captive<br>Toluene; partly captive                                    |
| Amoco Corporation<br>Amoco Oil Company, subsidiary   | Texas City, Texas                    | 85 (322)<br>25 (95)<br>12 (45)                | Catalytic reformat; partly captive<br>Pyrolysis gasoline; partly captive<br>Xylene isomerization |
| Aristech Chemical Corporation  | Clairton, Pennsylvania               | 45 (170)                                      | Coke-oven light oil  |
| Ashland Oil, Incorporated<br>Ashland Chemical Company, division<br>Petrochemicals Division | Catlettsburg, Kentucky               | 55 (208)<br>2 (8)                             | Coke-oven light oil; captive<br>Catalytic reformat; captive                                      |
| Atlantic Richfield Corporation<br>Lyondell Petrochemical Company, subsidiary               | Channelview, Texas<br>Houston, Texas | 90 (341)<br>35 (132)<br>15 (57)               | Pyrolysis gasoline; captive<br>Catalytic reformat; no captive use<br>Toluene; no captive use     |

(continued)

TABLE 4-1. CONTINUED

| Company Name  | Location                   | Annual Capacity<br>million gal<br>(million L) | Production Processes <sup>a</sup>  |
|---|----------------------------|---|------------------------------------|
| BP Oil  | Alliance, Louisiana        | 18 (68)                                       | Catalytic reformat; no captive use |
|   |                            | 47 (178)                                      | Toluene                            |
|   | Lima, Ohio                 | 35 (132)                                      | Catalytic reformat; no captive use |
|   |                            | 80 (303)                                      | Toluene                            |
| Chevron Corporation<br>Chevron Chemical Company, subsidiary<br>Aromatics and Derivatives Division | Philadelphia, Pennsylvania | 24 (91)                                       | Catalytic reformat; captive        |
|   |                            | 21 (79)                                       | Toluene; captive                   |
|   | Port Arthur, Texas         | 42 (159)                                      | Catalytic reformat; partly captive |
|   |                            | 24 (91)                                       | Pyrolysis gasoline; partly captive |
|   |                            | 35 (132)                                      | Toluene; partly captive            |
| Citgo Petroleum Corporation   | Corpus Christi, Texas      | 55 (208)                                      | Catalytic reformat; captive        |
|   |                            | 23 (87)                                       | Toluene                            |
| Coastal Eagle Point Oil Co.   | Westville, New Jersey      | 15 (57)                                       | Catalytic reformat                 |
| Coastal Refining and Marketing, Inc.  | Corpus Christi, Texas      | 50 (189)                                      | Toluene; captive use               |
|   |                            | 7 (26)  | Catalytic reformat                 |
| Dow Chemical U.S.A.   | Freeport, Texas            | 25 (95)                                       | Pyrolysis gasoline; captive        |
|   | Plaquemine, Louisiana      | 80 (303)                                      | Pyrolysis gasoline; captive        |
|   |                            | 120 (454)                                     | Toluene; captive                   |

(continued)

TABLE 4-1. CONTINUED

|    | Company Name   | Location               | Annual Capacity            | Production Processes <sup>a</sup>  |
|----|--|------------------------|----------------------------|------------------------------------|
|    |  |                        | million gal<br>(million L) |                                    |
| 44 | Exxon Corporation  | Corpus Christi, Texas  | 50 (189)                   | Pyrolysis gasoline                 |
|    | Exxon Chemical Company, division                           |                        | 30 (114)                   | Toluene                            |
|    | Exxon Chemical Americas                                    | Baton Rouge, Louisiana | 50 (189)                   | Catalytic reformat                 |
|    |  |                        | 30 (114)                   | Pyrolysis gasoline; no captive use |
|    |  | Baytown, Texas         | 75 (284)                   | Catalytic reformat; no captive use |
|    |  |                        | 20 (76)                    | Pyrolysis gasoline                 |
|    |  |                        | 20 (76)                    | Xylene isomerization               |
|    |  |                        | 23 (87)                    | Toluene                            |
|    | Huntsman Chemical Corporation                              | Bayport, Texas         | 15 (57)                    | Toluene; captive                   |
|    | Kerr-McGee Corporation                                     | Corpus Christi, Texas  | 17 (64)                    | Catalytic reformat; no captive use |
|    | Southwestern Refining Company,<br>Incorporated, subsidiary |                        |                            |                                    |
|    | Koch Industries, Incorporated                              | Corpus Christi, Texas  | 25 (95)                    | Catalytic reformat; captive        |
|    | Koch Refining Company, subsidiary                          |                        | 55 (208)                   | Toluene; captive                   |
|    |  |                        | 10 (38)                    | Xylene isomerization               |
|    |  |                        | 50 (189)                   | Toluene                            |
|    | Mobil Corporation  | Beaumont, Texas        | 90 (341)                   | Catalytic reformat; no captive use |
|    | Mobil Oil Corporation                                      |                        | 10 (38)                    | Pyrolysis gasoline                 |
|    | Mobil Chemical Company, division                           |                        | 20 (76)                    | Catalytic reformat; no captive use |
|    | Petrochemicals Division                                    | Chalmette, Louisiana   |                            |                                    |
|    | U.S. Marketing and Refining Division                       |                        |                            |                                    |

(continued)

TABLE 4-1. BENZENE PRODUCTION FACILITIES

| Company Name   | Location                                 | Annual Capacity<br>million gal<br>(million L) | Production Processes <sup>a</sup>  |
|--|--|---|--|
| Occidental Petroleum Corporation<br>Petrochemicals Olefins and Aromatics Division            | Chocolate Bayou, Texas                   | 60 (227)<br>40 (151)                          | Pyrolysis gasoline<br>Toluene  |
| Phibro Energy USA, Inc.  | Houston, Texas                           | 5 (19)  | Catalytic reformat; no captive use   |
| Phillips Petroleum Company<br>Chemicals Division<br>Olefins and Cyclics Branch               | Sweeny, Texas                            | 11 (42)                                       | Catalytic reformat; captive  |
| Phillips Puerto Rico Core, Incorporated, subsidiary  | Guayama, Puerto Rico                     | 35 (132)<br>48 (182)                          | Catalytic reformat; captive<br>Toluene; captive  |
| Shell Oil Company<br>Shell Chemical Company, division  | Deer Park, Texas<br>Wood River, Illinois | 75 (284)<br>80 (303)<br>50 (189)              | Catalytic reformat; partly captive<br>Pyrolysis gasoline; partly captive<br>Catalytic reformat; no captive use |
| Sun Company, Incorporated<br>Sun Refining and Marketing Company,<br>Incorporated, subsidiary | Marcus Hook, PA<br>Toledo, Ohio          | 26 (98)<br>11 (42)<br>19 (72)                 | Catalytic reformat; no captive use<br>Toluene; no captive use<br>Catalytic reformat                            |

(continued)

TABLE 4-1. BENZENE PRODUCTION FACILITIES

| Company Name                           | Location                | Annual Capacity<br>million gal<br>(million L) | Production Processes <sup>a</sup> |
|--|-------------------------|---|-----------------------------------|
| Texaco, Incorporated                   | El Dorado, Kansas       | 15 (57)                                       | Catalytic reformat; captive       |
| Texaco Chemical Company, subsidiary    | Port Arthur, Texas      | 46 (174)                                      | Catalytic reformat; captive       |
|  |                         | 20 (76)                                       | Pyrolysis gasoline; captive       |
| The UNO-VEN Company                    | Lemont, Illinois        | 12 (45)                                       | Catalytic reformat                |
|  |                         | 7 (26)  | Coke-oven light oil; no captive   |
| USX Corporation                        | Lake Charles, Louisiana | 55 (208)                                      | Catalytic reformat; captive       |
| Marathon Oil Company, subsidiary       | Texas City, Texas       | 7 (26)  | Toluene                           |
| Marathon Petroleum Company, subsidiary |                         |   |                                   |
| <b>TOTAL</b>                           |                         | <b>2,350(8,896)</b>                           |                                   |

Source: Reference 11.

<sup>a</sup> Captive means used for subsequent processes on site.

Note: This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables such as throughput and control measures, and should be determined through direct contacts with plant personnel. Reference SRI '93 indicates these data reflect changes made in product locations as of January 1993.

Production of benzene by reforming/separation is associated with the production of toluene and xylene (BTX plants). Catalytic reforming is used to prepare high-octane blending stocks for gasoline production and for producing aromatics as separate chemicals. The reforming process, shown in Figure 4-1,<sup>22</sup> accounts for about 45 percent of all benzene produced in the United States.<sup>12</sup> In the following description of the reforming process, potential emission points are identified; however, not all of the emission points discussed in this section are always present at plants using this production process. Some companies have indicated that they have closed systems; others have indicated that process vent emissions are well-controlled by flares or scrubbers.<sup>22</sup>

#### 4.1.1 Process Description for Catalytic Reforming/Separation

The reforming process used at BTX plants (shown in Figure 4-1) can greatly increase the aromatic content of petroleum fractions by such reactions as dehydrogenation, isomerization and dehydrogenation, or cyclization. The usual feedstock in this process is a straight-run, hydrocracked, thermally cracked, or catalytically cracked naphtha. After the naphtha is hydrotreated to remove sulfur (Stream 1), it is mixed with recycled hydrogen (Stream 4) and heated. This feed (Stream 2) is sent through catalytic reactors in which the catalyst, usually platinum or rhenium chloride, converts paraffins to aromatic compounds. The product stream (Stream 3) consists of excess hydrogen and a reformate rich in aromatics. Products from the reactor (Stream 3) are fed to the separation section, which separates the hydrogen gas from the liquid product. The hydrogen gas can be recycled to the reactor (Stream 4). The liquid product from the separator (Stream 5) is fed to a stabilizer (not shown in the figure).<sup>22</sup> The stabilizer is a fractionator in which more volatile, light hydrocarbons are removed from the high-octane liquid product. The liquid is then sent to a debutanizer (not shown in the figure). Aromatics (benzene, toluene, and mixed xylenes) are then extracted from the stabilized reformate.<sup>22</sup>

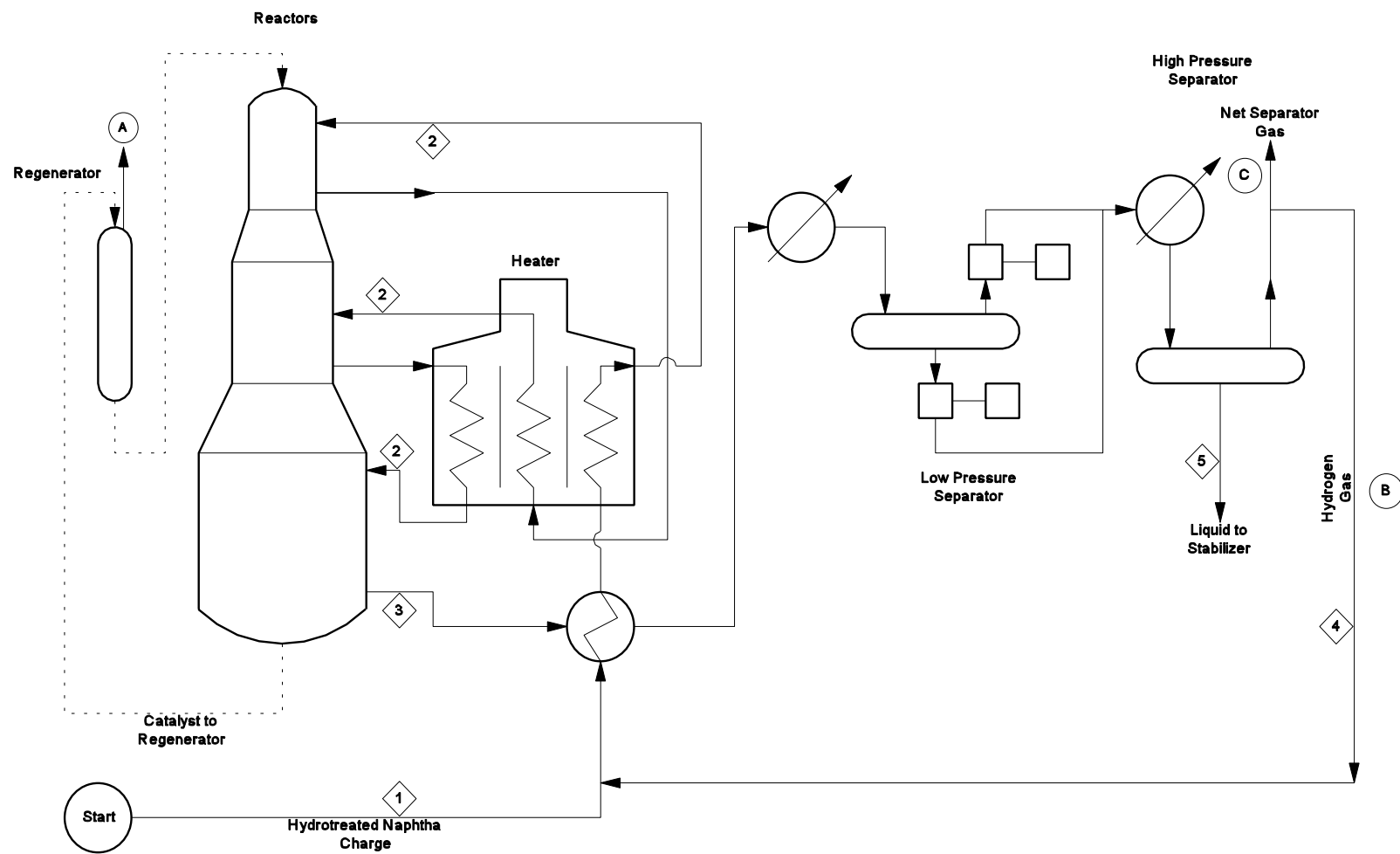


Figure 4-1. Universal Oil Products Platforming (Reforming) Process

Source: Reference 22.

Numerous solvents are available for the extraction of aromatics from the stabilized reformat stream. Glycols (tetraethylene glycol) and sulfolane (1,1-tetrahydrothiophene dioxide) are most commonly used. The processes in which these solvents are used are similar, so only the glycol process is described here. In the glycol process shown in Figure 4-2, aromatics are separated from the reformat in the extractor.<sup>22</sup> The raffinate (stream 2) is water-washed and stored. The dissolved aromatics extract (Stream 1) is steam-stripped and the hydrocarbons separated from the solvent. The hydrocarbon stream (Stream 3) is water-washed to remove remaining solvent and is then heated and sent through clay towers to remove olefins (Stream 4). Benzene, toluene, and xylene (Stream 5) are then separated by a series of fractionation steps.<sup>22</sup>

#### 4.1.2 Benzene Emissions from Catalytic Reforming/Separation

The available information on benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with benzene production using the catalytic reforming/separation process is presented below. Where a literature review revealed no source-specific emission factors for uncontrolled or controlled benzene emissions from these emission points from this process, the reader is referred to Section 4.5 of this chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these emission points.

A literature search, a review of materials in the docket (A-79-27) for some National Emission Standards for Hazardous Air Pollutants (NESHAP) efforts on benzene, and information provided by the benzene production industry revealed no source-specific emission factors for benzene from catalytic reforming/separation.<sup>22</sup> However, information provided by the benzene production industry indicates that BTX is commonly produced in closed systems, and that any process vent emissions are well-controlled by flares and/or scrubbers. (See Section 4.5 of this chapter for a discussion of control devices.)<sup>22</sup> Furthermore, some descriptive data were found, indicating that benzene may be emitted from the

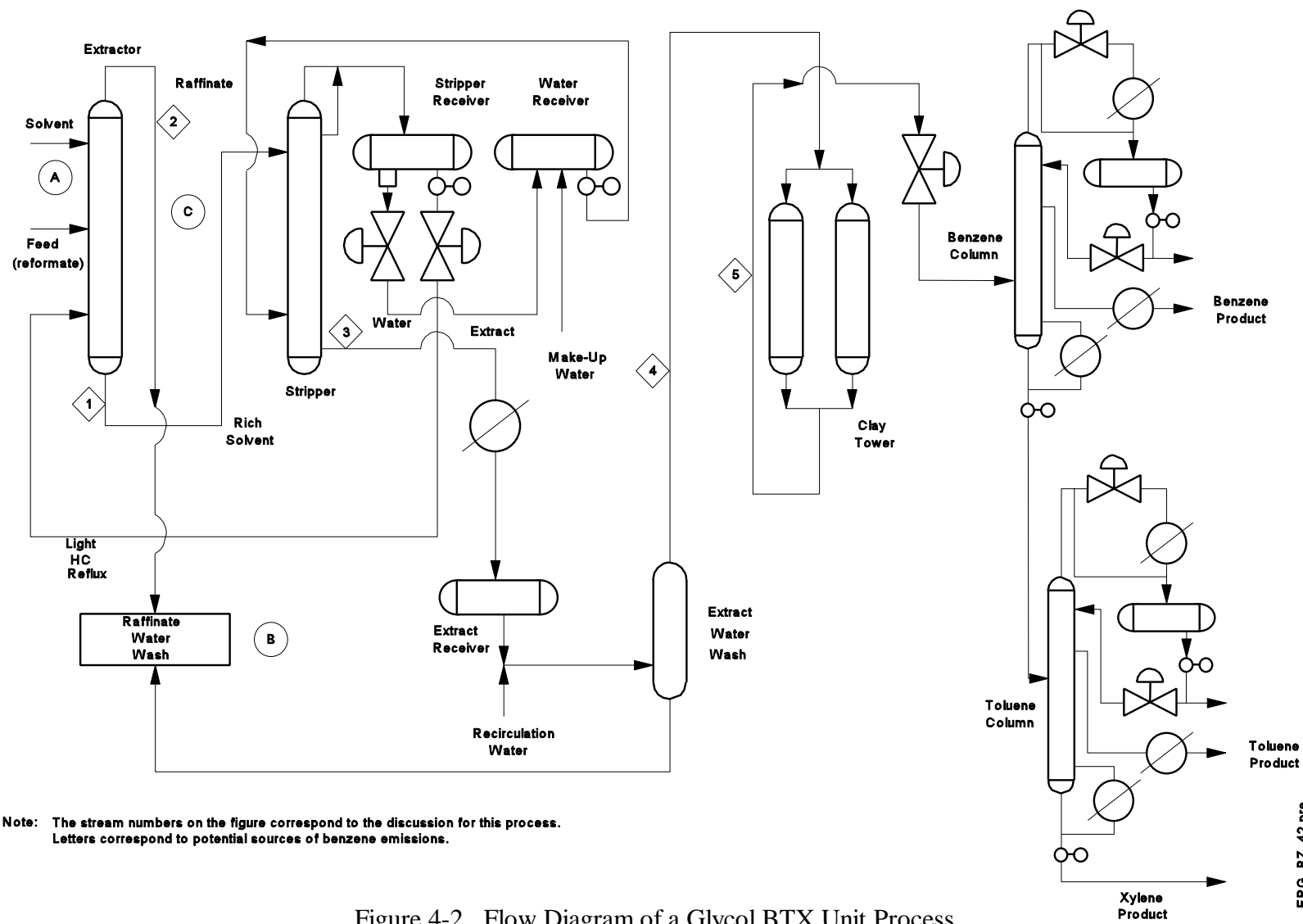


Figure 4-2. Flow Diagram of a Glycol BTX Unit Process

Source: Reference 22.

catalytic/reforming process during catalyst regeneration or replacement, during recycling of hydrogen gas to the reformer, and from the light gases taken from the separator. These potential emission points are labeled as A, B, and C, respectively, in Figure 4-1.

One general estimate of the amount of benzene emitted by catalytic reforming/separation has been reported in the literature. In this reference, it was estimated that 1 percent of total benzene produced by catalytic reforming is emitted.<sup>23</sup>

Benzene may be emitted from separation solvent regeneration, raffinate wash water, and raffinate in association with the separation processes following catalytic reforming. These potential sources are shown as A, B, and C, respectively, in Figure 4-2. However, no specific data were found showing emission factors or estimates for benzene emissions from these potential sources. One discussion of the Sulfolane process indicated that 99.9-percent recovery of benzene was not unusual. Therefore, the 0.1 percent unrecovered benzene may be a rough general estimate of the benzene emissions from separation processes.<sup>23</sup>

#### 4.2 TOLUENE DEALKYLATION AND TOLUENE DISPROPORTIONATION PROCESS

Benzene can also be produced from toluene by hydrodealkylation (HDA) or disproportionation. The amount of benzene produced from toluene depends on the overall demand and price for benzene because benzene produced by HDA costs more than benzene produced through catalytic reforming or pyrolysis gasoline.<sup>24</sup> At present, benzene production directly from toluene accounts for almost 30 percent of total benzene produced.<sup>11</sup> Growth in demand for toluene in gasoline (as an octane-boosting component for gasoline blending) appears to be slowing because of increased air quality legislation to remove aromatics from gasoline. (At present, gasoline blending accounts for 30 percent of the end use of toluene.) If toluene is removed from the gasoline pool to any great extent, its value is expected to drop because surpluses will occur. In such a scenario, increased use of toluene to produce benzene by HDA or disproportionation would be expected.<sup>24</sup> At present, production of benzene by the HDA and disproportionation processes accounts for 50 percent of toluene end use.

#### 4.2.1 Toluene Dealkylation

##### Process Description

Hydrodealkylation of toluene can be accomplished through thermal or catalytic processes.<sup>25</sup> The total dealkylation capacity is almost evenly distributed between the two methods.<sup>10</sup> As shown in Figure 4-3, pure toluene (92 to 99 percent) or toluene (85 to 90 percent) mixed with other heavier aromatics or paraffins from the benzene fractionation column is heated together with hydrogen- containing gas to 1,346 °F (730 °C) at a specified pressure (Stream 1) and is passed over a dealkylation catalyst in the reactor (Stream 2). Toluene reacts with the hydrogen to yield benzene and methane. The benzene may be separated from methane in a high-pressure separator (Stream 3) by flashing off the methane-containing gas.<sup>25</sup>

The product is then established (Stream 4), and benzene is recovered by distillation in the fractionalization column (Stream 5).<sup>10</sup> Recovered benzene is sent to storage (Stream 6). Unreacted toluene and some heavy aromatic by-products are recycled (Stream 7). About 70 to 85 percent conversion of toluene to benzene is accomplished per pass through the system, and the ultimate yield is 95 percent of the theoretical yield. Because there is a weight loss of about 23 percent, the difference in toluene and benzene prices must be high enough to justify use of the HDA process.

##### Benzene Emissions

The available information on benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with benzene production using the toluene dealkylation process was reviewed. No source-specific emission factors were found for benzene emissions from its production through dealkylation of toluene. The reader is referred to Section 4.5 of this

chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these emission points.

Potential sources of emissions from the dealkylation process include the separation of benzene and methane, distillation, catalyst regeneration, and stabilization.<sup>23</sup> These potential sources are shown as emission points A, B, C, and D respectively, in Figure 4-3.<sup>10,15,25</sup>

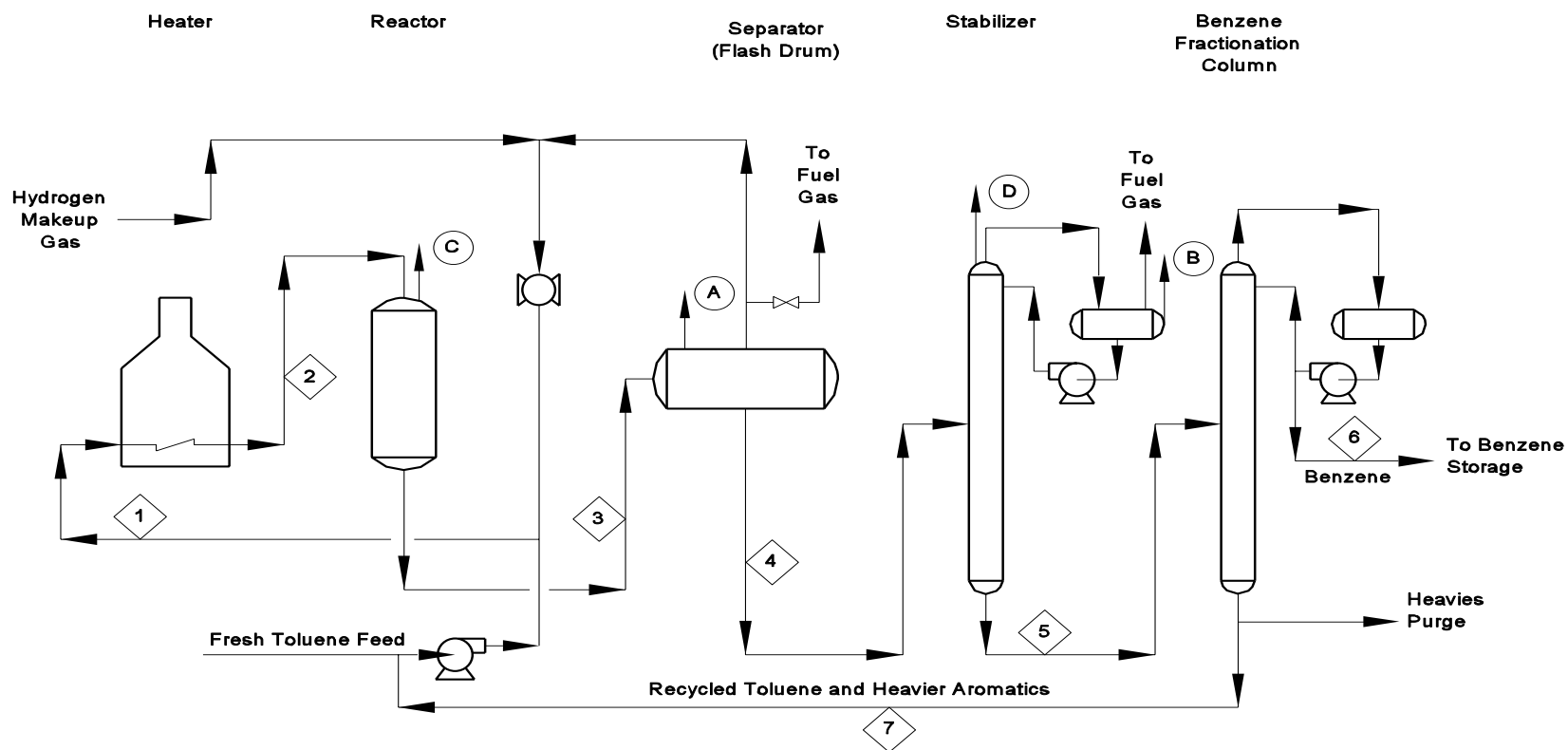
#### 4.2.2 Toluene Disproportionation

##### Process Description

Toluene disproportionation (or transalkylation) catalytically converts two molecules of toluene to one molecule each of benzene and xylene.<sup>24</sup> As shown in Figure 4-4, the basic process is similar to toluene hydrodealkylation, but can occur under less severe conditions.<sup>15,26</sup> Transalkylation operates at lower temperatures, consumes little hydrogen, and no loss of carbon to methane occurs as with HDA.<sup>24</sup> Toluene material is sent to a separator for removal of off-gases (Stream 3). The product is then established (Stream 4) and sent through clay towers (Stream 5). Benzene, toluene, and xylene are recovered by distillation, and unreacted toluene is recycled (Stream 6). Note that if benzene is the only product required, then HDA is a more economical and feasible process.<sup>27</sup>

##### Benzene Emissions

No specific emission factors were found for benzene emissions from its production via toluene disproportionation. Potential sources of benzene emissions from this process are associated with the separation of benzene and xylene, catalyst regeneration, and heavy hydrocarbons that do not break down.<sup>23</sup> These potential sources are shown as points A, B, and C, respectively, in Figure 4-4.



**Note:** The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-3. Process Flow Diagram of a Toluene Dealkylation Unit

Source: References 10, 15, and 25.

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Source: References 15 and 26.